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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with alkalinity, volatile acids and carbon dioxide determinations for an anaerobic sludge digester. Included are objectives, instructor guides, student handouts and transparency masters. This module considers total and bicarbonate alkalinity titration, percent carbon dioxide and digester gas by the carbon dioxide absorption methods and volatile acids concentration in digester sludge by the rapid distillation, the silicic acid, and the "Bach" Esterification methods. (Author/RH)

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ANAEROBIC DIGESTION ANALYSIS

Training Module 5.120.2.77

Prepared for the

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Des Moines, Iowa 50319

by

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September, 1977

SE 024 253

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Module No.	Module Title Anaerobic Digester Test Procedures
Approx. Time 12 hours	Topics Alkalinity Alkalinity Testing Determination of Alkalinity Digester Gas Analysis Volatile Acids Volatile Acids Testing Volatile Acids/Alkalinity Ratio Determination of Volatile Acids by Rapid Distillation Determination of Volatile Acids by Silicic Acid Method Determination of Volatile Acids by Hach Method Selection of Method for Volatile Acids Analysis

Objective

When the participants complete this module they should be able to analyze anaerobic digester contents for alkalinity and volatile acids and report the results as a volatile acids/alkalinity ratio. The participant should also be able to determine the amount CO_2 in digester gas upon completion of this module.

References

Anaerobic Sludge Digestion Manual (EPA)

Operation of Wastewater Treatment Plants (Kerri)

Standard Methods, 13th and 14th Eds.

Instructional Aids

EPA slide-tape is available from:

Eileen Hopewell
National Training Center
Water Programs Operation
Vine & St. Claire St.
Cincinnati, Ohio 45268

Overheads

Typed overheads are example of overhead layout and content. For classroon use the overhead should be constructed using colored, 1/4 inch dry transfer letters.

Other overheads may be copied directly.

Handouts`

Handouts may be copied directly.

Lab supplies and apparatus

Supplies and apparatus should be supplied per handouts so that participants may work in groups of 2 or 3.

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title:
Approx. Time: 30 Min.	Topic: Test Procedures

Objectives: When the participant completes this topic he should be able to:

1. Identify the type or class of material being analyzed in the alkalinity test, volatile acids test and digestor gas analysis test.
2. Identify the accepted units of expression for reporting results of the volatile acids test, alkalinity test and digester gas analysis test.
3. Indicate the range of concentrations of volatile acids, alkalinity and CO_2 in digester gas normally found in a properly operating digester.

Instructional Aids:

EPA slide tape - Anaerobic Digestion and Analytical Control

Instructional Approach:

Lecture - Discussion

References:

Anaerobic Sludge Digestion -

Class Assignments:

None

Module No:	Topic: Test Procedures
Instructor Notes:	Instructor Outline:
Slide Tape	1. a. Identify each of the tests and indicate the type of sample required. b. Discuss volatile acids, indicate how they are produced in a digestor and how they are used in the digester. c. Discuss alkalinity, indicate the sources of alkalinity in a digester. d. Discuss the components of digester gas. 2. a. Identify the standard units of expression for alkalinity, volatile acids and digester gas. 3. Identify the range of concentrations normally found in an operating digester. Volatile acids Alkalinity Gas

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Alkalinity
Approx. Time: 30 min.	Topic: Alkalinity Testing

Objectives: When the participant completes this topic he should be able to:

1. Define alkalinity
2. Indicate how alkalinity differs from pH
3. Identify the pH end-point of the total alkalinity titration.
4. Explain why a pH meter is preferred to a colored indicator end point.
5. Differentiate between total alkalinity and bicarbonate alkalinity.
6. State safety precautions to be observed in the alkalinity test.

Instructional Aids:

Handout - Alkalinity Discussion

Instructional Approach:

Lecture - Discussion

References:

Anaerobic Sludge Digestion Manual
Operation of Wastewater Treatment Plants (Kerri)

Class Assignments:

Module No:	Topic: Alkalinity Testing
Instructor Notes:	Instructor Outline:
Handout Pages 9 - 14 Alkalinity Discussion Page 7	1. Discuss alkalinity and how it is a measure of buffering capacity. 2. Explain how alkalinity differs from pH 3. Identify the pH end point of the total alkalinity test. Explain why this point is used. 4. Discuss the use of the pH meter for end point detection rather than a colored pH indicator. Explain that the colored pH indicator changes at the same pH as pH end point. 5. List the other types of alkalinity determinations.

TOTAL ALKALINITY

Discussion

Tests for total alkalinity of digesters are normally run on settled supernatant samples. The alkalinity of the recirculated sludge is a measure of the buffer in the digester. When organic matter in a digester is decomposed anaerobically, organic acids are formed which could lower the pH, if buffering materials (buffer capacity) were not present. If the pH drops too low, the organisms in the digester could become inactive or die and the digester becomes upset (no longer capable of decomposing organic matter).

For digester control purposes, the volatile acid/alkalinity relationship should be determined. When the volatile acid/alkalinity relationship is from less than 0.1/1.0 to 0.5/1.0, the loading and seed retention of the digester are under control. When the relationship starts increasing and becomes greater than 0.5/1.0, the digester is out of control and will become stuck unless effective corrective action is taken. The pH will not be out of range as long as the volatile acid/alkalinity relationship is low. This relationship gives a warning before trouble starts.

All samples must be settled so that a liquid free of solids is available for the test. Tests cannot be calculated correctly if solids are in the sample.

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Alkalinity
Approx. Time: 2 hours	Topic: Determination of Alkalinity

Objectives: When the participant completes this topic he should be able to:

1. Identify proper apparatus and reagents needed for the alkalinity test.
2. Obtain and prepare a proper sample for the alkalinity test.
3. Conduct an alkalinity test given proper test equipment, procedures sheet and proper sample material.
4. Translate the raw data from the alkalinity test into proper units of expression given appropriate conversion factors and equations.

Instructional Aids:

Handout - Determination of Alkalinity
Overhead Alkalinity Calculation
Lab apparatus and reagents per handout

Instructional Approach:

Lab

References:

Kerri

Class Assignments:

Lab procedure

Module No:	Topic: Determination of Alkalinity
Instructor Notes:	Instructor Outline:
Handout Determination of Alkalinity Pages 10 - 12	1. List the apparatus and reagents needed for the alkalinity test. Demonstrate the setup of apparatus. Demonstrate the makeup of reagents Discuss commercial reagents. 2. Discuss and if possible demonstrate proper sampling methods 3. Demonstrate the alkalinity test to include: pH meter standardization Titration technique Endpoint detection Have participants conduct an alkalinity test.
Overhead Alkalinity calculation Part 6 Page 10	4. Work an example calculation. Have particicipants work calculations

LABORATORY PROCEDURE: Alkalinity of Wastewater and Sludge

All samples must be settled so that a liquid free of solids is available for the test. Tests cannot be calculated correctly if solids are in the sample. All samples must be kept cool and analyzed as soon as possible.

Apparatus

1. Centrifuge and centrifuge tubes, or settling cylinder.
2. Graduated cylinders (25 ml and 100 ml).
3. 50 ml Burette.
4. 250 ml Erlenmeyer flask or 250 ml beaker.
5. pH meter

Reagents

For preparation consult Standard Methods or purchase prepared.

1. Sulfuric acid, 0.1 N, which is sufficient for alkalinities ranging from 500 - 6,000 mg/l.

Procedures

1. Centrifuge or filter about 100 mls. of supernatant sample.
2. Pipet 50 ml of sample into a beaker, in the case of water or distilled water use 100 ml sample. If digester alkalinity tends to be above 3,000 mg/l use a 25 ml. sample.
3. Add 200 ml. of distilled water.
4. Place the electrodes of pH meter into the 250 ml. beaker containing the sample.

5. Titrate to a pH of 4.5 with 0.10 N sulfuric acid. (In case of a lack of pH meter, add five drops of methyl orange indicator. In this case, titrate to the first permanent change of color to a red-orange color. Care must be exercised in determining the change of color and your ability to detect the change will improve with experience.)

6. Calculate alkalinity as mg/l $CaCO_3$.

Formula

$$\text{Alkalinity (mg/l)} = \frac{B \times N \times 50{,}000}{\text{mls of sample}}$$

Where B = mls of H_2SO_4 required to titrate sample to pH 4.5

N = Normality of H_2SO_4, i.e. 0.1 N

Calculation Example

Where B = 38.0 mls

N = 0.10

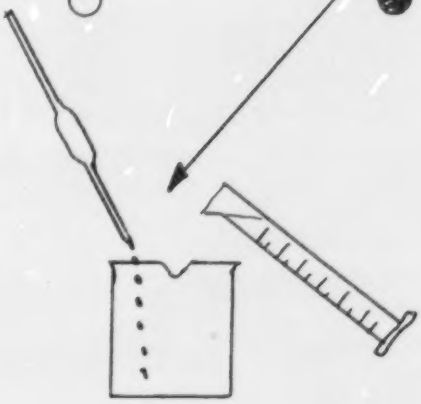
Sample size = 100 mls.

$$\text{Alkalinity (mg/l)} = \frac{38.0 \times 0.1 \times 50{,}000}{100}$$

OUTLINE OF METHOD

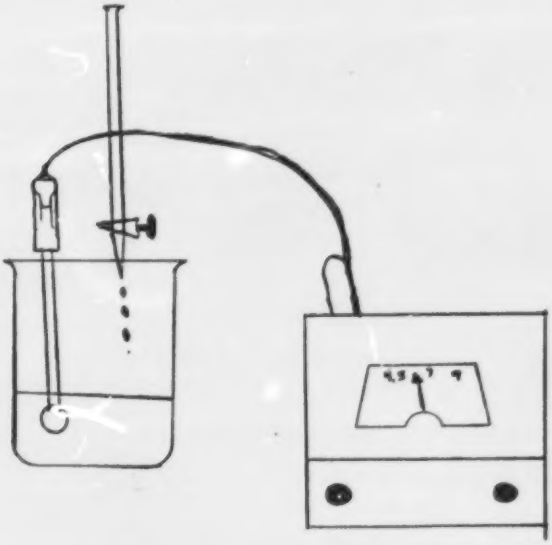
1. Remove solids by centrifuging

2. Pipet 50 ml of sample into a beaker



3. Add 200 ml of distilled water

4. Place pH electrodes in beaker



5. Titrate with 0.10 N acid

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title:
Approx. Time: 1 hour	Topic: Digester Gas Analysis by CO_2 Absorption

Objectives: When the participant completes this topic he should be able to:

1. Identify the proper apparatus and reagents needed for the digester gas analysis by CO_2 absorption test.
2. Obtain and prepare a proper sample for the test.
3. Conduct gas analysis test given proper test equipment, reagents, procedures sheet and sample.
4. Translate the raw data from the gas analysis test into proper units of expression given appropriate conversion factors and equations.

Instructional Aids:

Handout - Digester Gas Analysis
Lab Apparatus and Reagent per handout
Overhead Sample Calculation

Instructional Approach:

Lab

References:

Kerri

Class Assignments:

Lab procedure

Module No:	Topic: Digester Gas Analysis by CO_2 Absorption
Instructor Notes:	Instructor Outline:
Handout Digester Gas Analysis Pages 15 - 18	1. List the apparatus and reagents needed for digester gas analysis. Demonstrate the makeup of reagents and the use of apparatus. 2. Discuss sample collection and if possible demonstrate sample collection. 3. Demonstrate the gas analysis test. Have participant perform the test.
Overhead Sample calculation Part 11 Page 17	4. Work a sample calculation Have participant work calculations.

CARBON DIOXIDE (CO_2) IN DIGESTER GAS

Discussion

Changes in the anaerobic sludge digestion process will be observed in the gas quality and are usually noted after the volatile acids or volatile acid/alkalinity relationship starts to increase. The CO_2 content of a properly operating digester will range from 30% to 40% by volume. If the percent is above 44%, the gas will not burn. The easiest test procedure for determining this change is with a CO_2 analyzer.

Apparatus

1. One bunsen burner
2. Plastic tubing
3. 100 ml graduated cylinder
4. 250 ml beaker

Reagents

CO_2 absorbant (KOH). Add 500 g potassium hydroxide (KOH) per liter of water.

(CO_2)

Procedure

1. Measure total volume of a 100 ml graduate by filling it to the top with water (approximately 125 ml). Record this volume.
2. Pour approximately 125 ml of CO_2 absorbent in a 250 ml beaker.
   CAUTION: Do not get any of this chemical on your skin or clothes. Wash immediately with running water until slippery feeling is gone or severe burns can occur.
3. Collect a representative sample of gas from the gas dome on the digester, a hot water heater using digester gas to heat the sludge, or any other gas outlet. Before collecting the sample for the test, attach one end of a gas hose to the gas outlet and the other end to a bunsen burner. Turn on the gas, ignite the burner, and allow it to burn digester gas for a sufficient length of time to insure collecting a representative gas sample.
4. With gas running through hose from gas sampling outlet, place hose inside inverted calibrated graduated cylinder and allow digester gas to displace air in graduate. Turn off gas.
   CAUTION: The proper mixture of digester gas and air is explosive when exposed to a flame.
5. Place graduate full of digester gas upside down in beaker containing CO_2 absorbent.
6. Insert gas hose inside upside down graduate.
7. Turn on gas, but do not blow out liquid. Run gas for at least 60 seconds.
8. Carefully remove hose from graduate with gas still running.
9. Immediately turn off gas.
10. Wait for ten minutes and shake gently. If liquid continues to rise, wait until it stops.

11. Read gas remaining in graduate to nearest ml. (Fig. 14.3)

Example

Total volume of graduate = 126 ml

Gas remaining in graduate = 80 ml

Calculation

$$\% \, CO_2 = \frac{(\text{Total Volume, ml} - \text{Gas Remaining, ml})}{\text{Total Volume, ml}} \times 100\%$$

$$= \frac{(126 \text{ ml} - 80 \text{ ml})}{126 \text{ ml}} \times 100\%$$

$$= \frac{46}{126} \times 100\%$$

```
        .365
126/ 46.0
     37 8
      8 20
      7 56
        640
        630
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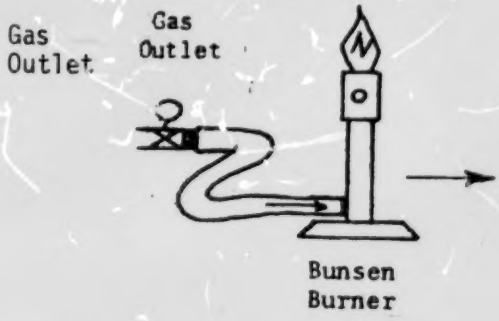
= 37%

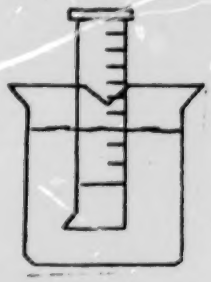
Outline of Procedure

1. Clean out sampling line by allowing gas from sampling outlet to burn until line is full of gas from digester.

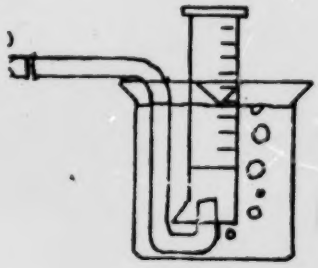


2. Displace air in graduated cylinder.

3. Place graduate upside down in beaker containing CO_2 absorbent.

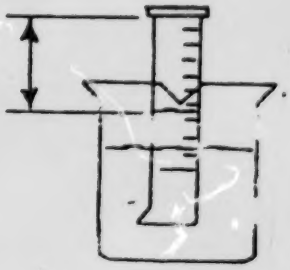


Insert hose in graduate and run gas for 60 seconds



5. Remove hose from graduate and then turn off gas. Wait 10 minutes

6. Find volume of gas remaining to nearest ml.



Precautions

1. Avoid any open flames near the digester.
2. Work in a well ventilated area to avoid the formation of explosive mixtures of methane gas.
3. If your gas sampling outlet is on top of your digester, turn on outlet and vent the gas to the atmosphere for several minutes to clear the line of old gas Start with Step 2, displace air in graduated cylinder.

NEVER ALLOW ANY SMOKING OR FLAMES NEAR THE DIGESTER AT ANY TIME.

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 30 Min.	Topic: Volatile Acids Testing

Objectives: When the participant completes this topic he should be able to:

1. Identify acidic, proponoic and buteric acids as the major contributers to the volatile acids concentration in a digester.
2. Differentiate between volatile acids and strong inorganic acids.
3. Explain why the volatile acids test should be run on the same sample as the alkalinity test.
4. Indicate that there are more than three ways to run a volatile acids test.

Instructional Aids:

Handout - Discussion of Volatile Acids

Instructional Approach:

Lecture - Discussion

References:

Kerri

Class Assignments:

None

Module No:	Topic: Volatile Acids Testing
Instructor Notes:	Instructor Outline:
Handout Discussion of Volatile Acids Page 21 - 22	1 & 2. Discuss the types of acids that make up volatile acids. Differentiate between volatile acids and strong inorganic acids. 3. Explain why the same sample should be used for the alkalinity test and volatile acids test. 4. List and summarize the three methods covered in the module. Indicate that there are other common methods. Discuss the need to use a single method and do it the same way each time.

VOLATILE ACIDS AND TOTAL ALKALINITY

Discussion

Volatile acids are determined on sludge samples from the digesters. Most modern digesters have sampling pipes where you can draw a sample from various levels of the tank. Be sure to allow the sludge in the line to run for a few minutes in order to obtain a representative sample of the digester contents. Samples also may be collected from supernatant draw-off tubes, or thief holes.[1]

The concentration of volatile acids and alkalinity are the first measurable changes that take place when the process of digestion is becoming upset. The volatile acid/alkalinity relationship can vary from 0.1 to about 0.5 without significant changes in digester performance. When the relationship starts to increase, this is a warning that undesirable changes will occur unless the increase is stopped. If the relationship increases above 0.5, the composition of the gas produced can change very rapidly, followed by changes in the rate of gas production, and finally pH.

In a healthy and properly functioning digester, the processes or biological action taking place inside the digester are in equilibrium. When fresh sludge is pumped into a digester, some of the organisms in the digester convert this material to volatile (organic) acids. In a properly operated digester, other organisms feed on the newly produced volatile acids and eventually convert the acids to methane (CH_4) gas, which is burnable and carbon dioxide (CO_2). If too much raw sludge is pumped to the digester or the digester is not functioning properly, an excess of volatile acids are

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[1] Thief Hole. A digester sampling well.

produced. If excessive amounts of volatile acids are produced, an acid environment unsuitable for some of the organisms in the digester will develop and the digester may cease to function properly unless the alkalinity increases too.

Routine volatile acids and alkalinity determinations during the start-up process for a new digester are a must in bringing the digester to a state of satisfactory digestion.

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 30 Min.	Topic: Volatile Acids - Alkalinity Ratio

Objectives: When the participant completes this topic he should be able to:

1. Calculate a volatile acids - alkalinity ratio.
2. Indicate the range of acceptable volatile acids - alkalinity ratios from a properly operating digester.
3. Develop a volatile acids - alkalinity trend graph and explain why a volatile acids - alkalinity ratio trend is of more value than a single volatile acids - alkalinity value.
4. Indicate why data from the volatile acids and alkalinity tests are of more value in digester operation than pH values.

Instructional Aids:

Overhead Volatile Acids Alkalinity Ratio Calculation

Instructional Approach:

Lecture - Discussion

References:

Kerri

Class Assignments:

None

Module No:	Topic: Volatile Acids - Alkalinity Ratio
Instructor Notes:	Instructor Outline:
Overhead Volatile acid/alkalinity ratio	1. Demonstrate how to calculate a volatile acids alkalinity ratio. 2. List the normal range of VA/Alk ratios. Discuss what may be the consequences of higher and lower than normal ranges. 3. Demonstrate the graphing of data. Discuss the importance of observing trends. 4. Discuss the falacy of using pH as a process control test.

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 2 hours 30 Min.	Topic: Determination of Volatile Acids by Rapid Distillation

Objectives: When the participant completes this topic he should be able to:

1. Identify proper apparatus and reagents needed for the volatile acids test by rapid distillation method.
2. Obtain and prepare a proper sample for the volatile acids test.
3. Conduct a volatile acids test using the rapid distillation method given proper test equipment, reagents, procedures sheet and sample.
4. Translate the raw data from the volatile acids test into proper units of expression given appropriate conversion factors and equations.

Instructional Aids:

Handout Distillation Method
Lab apparatus and reagents per handout

Instructional Approach:

Lab

References:

Standard Methods, 13th Ed.

Class Assignments:

Perform analysis in groups

Module No:	Topic: Rapid Distillation Method
Instructor Notes:	Instructor Outline:
Handout Rapid Distillation Method Pages 27 - 28	1. List the apparatus and reagents needed for the rapid distillation method. Demonstrate the makeup of reagents and setup of apparatus. 2. Discuss sample collection 3. Demonstrate the start and end of the distillation. Have participant perform the test. 4. Work a sample calculation Have participant work calculations

DISTILLATION METHOD

General Discussion

The following short method often is applicable for control purposes. Because the method is empiracal it should be carried out exactly as described. It is assumed that 70% of the volatile acids will be found in the distillate. This is corrected for in the computations. However, this factor has been found to vary from 68 to 85%, depending on the nature of the acids and the rate of distillation.

Apparatus

a. Centrifuge, with head to carry four 50-ml tubes or 250-ml bottles.

b. Distillation flask, 500-ml capacity.

c. Condenser, about 76 cm (30 in.) in length.

d. Adapter tube.

Reagents

a. Sulfuric acid, H_2SO_4, 1 + 1.

b. Standard sodium hydroxide titrant, 0.1 N.

c. Phenolphthalein indicator solution.

Procedure

Centrifuge 200 ml sample for 5 min. Pour off and combine the supernatant liquors. Place 100 ml supernatant liquor in a 500-ml distillation flask. Add 100 ml distilled water, 4 to 5 clay chips or similar material to prevent bumping, and 5 ml H_2SO_4. Mix so that the acid does not remain on the bottom of the flask. Connect the flask to a condenser and adapter tube and distill at the rate of about 5 ml/min. Collect 150 ml distillate in a

250-ml conical flask and titrate with 0.1 N NaOH, using phenolophthalein as an indicator. The endpoint is the first pink coloration that persists on standing a short time. Titration at 95 C produces a stable endpoint.

Calculations

mg/l volatile acids as acetic acid =

$$\frac{B \times N \times 60{,}000}{\text{Sample size} \times 0.7}$$

B = mls of base used

N = Normality of base used

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 2 hours	Topic: Determination of Volatile Acids by Silicic Acid Method

Objectives: When the participant completes this topic he should be able to:

1. Identify proper apparatus and reagents needed for the volatile acids test by silicic acid method.
2. Obtain and prepare a proper sample for the volatile acids test.
3. Conduct a volatile acids test using the silicic acid method given proper test equipment, reagents, procedures sheet and sample.
4. Translate the raw data from the volatile acids test into proper units of expression given appropriate conversion factors and equations.

Instructional Aids:

Handout Silicic Acid Method
Lab apparatus and reagents per handout
Overhead sample calculation

Instructional Approach:

Lab

References:

Standard Methods, 14th Ed.
Kerri

Class Assignments:

Perform analysis

Module No:	Topic: Silicic Acid Method
Instructor Notes:	Instructor Outline:
Handout Volatile Acids Silicic Acid Method Pages 31 - 35	1. List the apparatus and reagents needed for silicic acid method. Demonstrate the makeup of reagents and setup of apparatus. 2. Discuss sample collection and if possible demonstrate sample collection. 3. Demonstrate the silicic acid method for volatile acids. Have participant perform the test.
Overhead Sample Calculations Example Page 34	4. Work a sample calculation. Have participant work calculations

VOLATILE ACIDS

(Silic Acid Method)

Apparatus

1. Centrifuge or filtering apparatus.
2. Two 50 ml graduated cylinders.
3. Two mdeicine droppers.
4. Crucibles, Gooch or fritted glass
5. Filter flask
6. Vacuum source
7. One 50 ml beaker
8. Two 5 ml pipettes
9. Buret

Reagents

1. Silicic acid, solids, 100-mesh. Remove fines from solid portion of acid by slurrying the acid in distilled water and removing the supernatant after allowing settling for 15 minutes. Repeat the process several times. Dry the washed acid solids in an oven at 103° C and then store in a desiccator.
2. Chloroform - butanol reagent. Mix 300 ml chloroform, 100 ml N-butanol, and 80 ml 0.5 N H_2SO_4 in separatory funnel and allow the water and organic layers to separate. Drain off the lower organic layer through filter paper into a dry bottle.
3. Thymol blue indicator solution. Dissolve 80 mg thymol blue in 100 ml absolute methanol.
4. Phenolphthalein indicator solution. Dissolve 80 mg phenolphthalein in 100 ml absolute methanol.
5. Sulfuric acid, 10 N.

6. Standard sodium hydroxide reagent, 0.02 N. Prepare in absolute methanol from conc. NaOH stock solution in water.

Procedure

1. Centrifuge or filter enough sludge to obtain a sample of 10 to 15 ml. This same sample and filtrate should be used for both the volatile acids test and the total alkalinity test.
2. Measure volume (10 to 15 ml) of sample and place in a beaker.
3. Add a few drops of thymol blue indicator solution.
4. Add 10 N H_2SO_4, dropwise, until thymol blue color just turns to red.
5. Place 10 grams of silicic acid (solid acid) in crucible and apply suction. This will pack the acid material and the packed material is sometimes called a column.
6. With a pipette, distribute 5.0 ml acidified sample (from Step 4) as uniformly as possible over the column. Apply suction briefly to draw the acidified sample into the silicic acid column. Release the vacuum as soon as the sample enters the column.
7. Quickly add 50 ml chloroform-butanol reagent to the column.
8. Apply suction and stop just before the last of the reagent enters the column.
9. Remove the filter flask from the crucible.
10. Add a few drops of phenolphthalein indicator solution to the liquid in the filter flask.

11. Titrate with 0.02 N NaOH titrant in absolute methanol, taking care to avoid aerating the sample. Nitrogen gas of CO_2 - free air delivered through a small glass tube may be used both to mix the sample and to prevent contact with atmospheric CO_2 during titration (CO_2 - free air may be obtained by passing air through ascarite or equivalent).
    Volume of NaOH used in sample titration, a = _____ml.
12. Repeat the above procedure using a blank of distilled water.
    Volume of NaOH used in blank titration, b = _____ml.

Precautions

1. The sludge sample must be representative of the digester. The sample line should be allowed to run for a few minutes before the sample is taken. The sample temperature should be as warm as the digester itself.
2. The sample for the volatile acids test should not be taken immediately after charging the digester with raw sludge. Should this be done, the raw sludge may short-circuit to the withdrawal point and result in the withdrawal of raw sludge rather than digested sludge. Therefore, after the raw sludge has been fed into the tank, the tank should be well mixed by recirculation or other means before a sample is taken.
3. If a digester is performing well with low volatile acids and then if one sample should unexpectedly and suddenly give a high value, say over 1000 mg/l of volatile acids, do not become alarmed. The high result may be caused by a poor, nonrepresentative sample of raw sludge instead of digested sludge. Resample and retest. The second test may give a more typical value. When increasing volatile acids and decreasing alkalinity

are observed, this is a definite warning of approaching control problems. Corrective action should be taken immediately, such as reducing the feed rate, reseeding from another digester, maintaining optimum temperatures, improving digester mixing, decreasing sludge withdrawal rate, or cleaning the tank of grit and scum.

Example

Equivalent Weight of Acetic Acid, A = 60 mg/ml

Volume of Sample, B = 10 ml

Normality of NaOH titrant, N = 0.02 N

Volume of NaOH used in sample titration, a = 2.3 ml

Volume of NaOH used in blank titration, b = 0.5 ml

Calculation

$$\text{Volatile Acids, mg/l} = \frac{A \times 1000\ \text{ml/l} \times N\ (a - b)}{B}$$

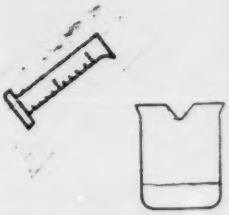
$$= \frac{60\ \text{mg/ml} \times 1000\ \text{ml/l} \times 0.02\ (2.3\ \text{ml} - 0.5\ \text{ml})}{10\ \text{ml}}$$

$$= 216\ \text{mg/l}$$

OUTLINE OF METHOD

1. Remove solids by centrifuging

2. Measure 10-15 ml of sample into a beaker



3. Add a few drops of thymol blue

4. Add 10 N H_2SO_4 dropwise untill thymol blue turns red

5. Place about 10 g of silic acid in crucible and apply suction

6. Add 5.0 ml of acidified sample

7. Add 50 ml of chloroform butanol reagent

8. Apply suction untill all of the reagent has entered the column

9. Remove the filter flask

10. Add phenolphthalein and titrate with 0.02 N NaOH

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 2 hours	Topic: Determination of Volatile Acids by "Hach" Method

Objectives: When the participant completes this topic he should be able to:

1. Identify proper apparatus and reagents needed for the volatile acids test by Hach method.
2. Obtain and prepare a proper sample for the volatile acids test.
3. Conduct a volatile acids test using the Hach method given proper test equipmen reagents, procedures sheet and sample
4. Translate the raw data from the test into proper units of expression given appropriate conversion factors and equations.

Instructional Aids:

Handout - Hach Method

Instructional Approach:

Lab

References:

Procedures, Chemical Lists and Glassware for Water and Wastewater with Calabration Table.

3rd Ed. Hach Chemical Co.

Class Assignments:

Perform analysis

Module No:	Topic: Hach Method
Instructor Notes:	Instructor Outline:
Handout Hach Method Pages 38 - 39	1. List the apparatus and reagents needed for the Hach method. 2. Discuss sample collection. 3. Demonstrate the test Have participant perform the test. 4. Calculate results from tables provided by Hach.

VOLATILE ACIDS

Esterification Method for Digestor Sludge

The Volatile Acids test is designed specifically for the determination of volatile organic acids in digestor sludge. All volatile acids present are reported as their equivalent mg/l acetic acid. Materials commonly present in digestor sludge do not interfere with the test.

Sample Preparation

1. Pipet 0.5 ml of demineralized water into a clean, dry DR-2 sample cell.
2. Clarify a few ml of the sample by filtration or centrifuging and pipet 0.5 ml of the filtrate or clear supernatant into a second clean, dry DR-2 sample cell.
3. Pipet 1.5 ml of Ethylene Glycol into each cell and swirl to mix.
4. Using a pipet filler, pipet 0.2 ml of 19.2 N Sulfuric Acid Standard Solution into each cell and swirl to mix. DO NOT PIPET BY MOUTH.
5. Place both cells in a boiling water bath for 3 minutes, then cool immediately in tap water.
6. Pipet 0.5 ml of Hydroxylamine Hydrochloride Solution into each cell and swirl to mix.
7. Using a pipet filler, pipet 2.0 ml of 4.5 N Sodium Hydroxide Standard Solution into each cell and swirl to mix. DO NOT PIPET BY MOUTH.
8. Add 10 ml of Ferric Chloride--Sulfuric Acid Solution to each of the two sample cells using a 10-ml graduated cylinder.
9. Add 10 ml of demineralized water to each sample cell using a 10-ml graduated cylinder and swirl to mix. Allow at least 3 minutes for the solutions to stabilize before taking the reading.
10. Adjust the Wavelength Control to 495 nm.

11. Cover the empty sample compartment and adjust the Zero Control for a reading of exactly zero % T.

12. Place a ½ inch test tube containing the treated demineralized water into the sample compartment and adjust the Full Scale Control for a meter reading of exactly 100 % %.

13. Place a ½ inch test tube containing the treated sample water into the sample compartment and read the percent transmittance. Refer to the following table to determine the mg/l volatile acids (as acetic acid).

Concentration vs. % Transmittance
% T Units

%T Tens	0	1	2	3	4	5	6	7	8	9
10	5600	5370	5160	4960	4785	4615	4460	4310	4170	4040
20	3915	3795	3685	3575	3470	3370	3275	3185	3095	3015
30	2930	2850	2770	2700	2625	2555	2485	2420	2350	2290
40	2230	2165	2110	2055	2000	1945	1885	1835	1785	1735
50	1690	1635	1590	1550	1500	1455	1410	1365	1325	1280
60	1245	1200	1165	1125	1085	1045	1015	974	941	902
70	870	835	795	778	734	700	666	638	605	571
80	543	515	482	454	426	398	370	342	314	286
90	258	230	202	179	151	123	101	73	50	22

Module No:	Module Title: Anaerobic Digester Test Procedures
	Submodule Title: Volatile Acids
Approx. Time: 30 Min.	Topic: Selection of Method for Volatile Acids Analysis

Objectives: When the participant completes this topic he should be able to:

1. Differentiate between the three volatile acids test methods as covered in preceding topics by comparing the following parameters:

   Time required to complete the test
   Equipment and reagents required
   Precision and accuracy
   Interferences encountered

2. Recommend a volatile acids test method using the above parameters for use in "Home" plant.

Instructional Aids:

None

Instructional Approach:

Discussion

References:

Class Assignments:

Select method
Take final test

Module No:	Topic: Selection of Method
Instructor Notes:	Instructor Outline:
	1. Discuss with participant the three methods for volatile acids. Time Equipment Reagents Precision Accuracy Interferences 2. Have participants select a method best for his or her individual needs and facilities. 3. Take final test.